Inhibition of Pipelines Corrosion Using Natural Extracts

Eman Alzahrani, Hala M. Abo-Dief, Ashraf T. Mohamed

Abstract**—**The present work is aimed at examining carbon steel oil pipelines corrosion using three natural extracts (Eruca Sativa, Rosell and Mango peels) that are used as inhibitors of different concentrations ranging from 0.05-0.1wt. %. Two sulphur compounds are used as corrosion mediums. Weight loss method was used for measuring the corrosion rate of the carbon steel specimens immersed in technical white oil at 100ºC at various time intervals in absence and presence of the two sulphur compounds. The corroded specimens are examined using the chemical wear test, scratch test and hardness test. The scratch test is carried out using scratch loads from 0.5 Kg to 2.0 Kg. The scratch width is obtained at various scratch load and test conditions. The Brinell hardness test is carried out and investigated for both corroded and inhibited specimens. The results showed that three natural extracts can be used as environmentally friendly corrosion inhibitors.

Keywords**—**Inhibition, natural extract, pipelines corrosion, sulphur compounds.

I. INTRODUCTION

CARBON steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali, and salt solutions [1]. It is widely used in most of the chemical industries due to its low cost and easy availability for fabrication of various reaction vessels, tanks, and pipes [2]. Transmission gas pipelines are an important part of energy-transportation infrastructure to the national economy. The prevention of failures and continued safe operation of these pipelines are therefore of national interest. These lines are mostly buried, protected and maintained by protective coating and cathodic protection systems, supplemented by periodic inspection equipped with sensors for inspection [3]. Ashraf and Abo-Dief [4] showed that there are two types of corrosion namely uniform corrosion and localized corrosion. Uniform corrosion usually occurs in environments where the corrosion rate is inherently low controlled or well controlled such as for chemically treated in closed circulating systems, and in some opens water systems. Localized corrosion is defined as the selective removal of metal by corrosion on small areas, zones, or on a metal surface, which comes into contact with a corrosive environment. It takes place when small local sites are attacked at a much higher rate than the rest of original surface. There are several types of localized corrosion; they are pitting corrosion, crevice corrosion, erosion corrosion, galvanic corrosion, cavitation's, fretting corrosion and intergranular attack corrosion. In this study, pitting corrosion will be highlighted [5], [6]. Patel et al. [7] concluded that corrosion is the chemical or electrochemical phenomenon that destroys the steel properties when exposed to aggressive species. Wear unlike corrosion destroys metal through removal of their surfaces mechanically. Corrosion-wear is an accelerated means of destroying metals by the combined influence of chemical/electro/chemical mechanism of corrosion and the mechanical effect of wear [8].

Corrosion inhibitors are chemicals that react with a metallic surface, or the environments that the metal surface is exposed to and act to protect the metal against corrosion [9]. The unique advantage of using natural products for the inhibition of the corrosion of metals is that they are environmentally friendly. Liang [10] designed the theoretical elucidation of the mild steel tube corrosion growth mechanism that occurred due to the effect of pH value and oxygen corrosion at elevated pressure. Parameswari et al. [11] investigated four heterocyclic compounds, and their influence on the inhibition of corrosion in 1 M H_2SO_4 by means of weight loss, potentiodynamic polarization, electrochemical impedance (EIS) and scanning electron microscopy (SEM).

The aim of the present work is to discuss the effect of Dimethylthiourea, and Dymethyl sulphoxide of different compositions and concentrations on the petroleum oil corrosion. The effect of the natural inhibitors (Eruca Sativa, Rosell and Mango peels) on the corroded specimens was examined using the weight loss method and both the scratch and hardness tests. The effect of both the corrosion mediums and natural inhibitors on the mild steel specimen surface is investigated at various test conditions is carried out using SEM examination.

II. EXPERIMENTAL DETAILS

Each carbon steel tube was prepared by mechanically pressed into sheets of 2 mm thickness. The carbon steel sheet was mechanically cut into specimens of 20 mm length and 10 mm width, having a hole of 2 mm uniform diameter to facilitate suspension in the test solution. The specimens were mechanically cleaned followed by grinding with emery paper of 600±1200 grit, and finally polished with a diamond paste of fine quality to expose shining polished surface. To remove any oil and organic impurities, they were degreased in absolute ethanol, dried in acetone and stored in moisture-free desiccators prior to use. Accurate weight of the samples was

Eman Alzahrani is with the Department of Chemistry, Faculty of Science, Taif University, Taif, KSA (e-mail: em-s-z@hotmail.com).
Hala M. Abo-Dief is with the Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt and the Department of Chemistry, Faculty of Science, Taif University, Taif, KSA (e-mail: mohamed.hala9173 @yahoo.com).
Ashraf T. Mohamed is with the Mechanical Engineering Dept., Faculty of Eng., Al-Baha, KSA (e-mail: profasht@yahoo.com).

taken using electronic balance. Triple experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed calculation of the mean corrosion rate. Micrographs of the corroded and corrosion inhibited mild steel surface specimens are taken. The tested specimens were hung by using glass hooks in a beaker contained 300 mL of the test solution of technical white oil at 100ºC containing 0.4 mg and 0.8 mg of both dimethyl thiourea (DTU), and dimethyl sulfoxide (DSO) (sulphur compounds) at time periods of 15, 30, 45, and 60 days. The corrosion product was removed by immersing the specimens for 2 min in a pickling solution containing thiourea (1g L^{-1}) in 10% H_2SO_4, then washed with distilled water and acetone, dried and weighed. Stock solutions of the inhibitors (Eruca Sativa, Rosell and Mango peels) were prepared by extracting 50 g of the dried and crushed materials with about 300 mL of boiling distilled water. The procedure was repeated four times and the collected extract was allowed to stand overnight, filtered through ordinary filter paper, and concentrated to 500 mL. The extracts were kept in the ice chest. From this solution, different concentrations of inhibitor solutions ranging from 0.05 to 0.1% were diluted. They also preserved at room temperature in the presence of 0.1% sodium benzoate. After the specified times, the specimens were removed from test solution, thoroughly washed with $NaHCO_3$ solution and de-ionized water, dried well and then weighed. The percentage of inhibitor efficiency (IE %) for various concentrations of the inhibitor were calculated [6] as;

$$\text{I.E. \%} = [(W_1 - W_2)/W_1] \times 100 \tag{1}$$

where, W_1 and W_2 = Weight loss without and with inhibitor.

The scratch hardness measurement was used to demonstrate the greater degree of anisotropy observed in single crystals compared with the indentation technique. The general aims of the scratch test are to clarity the mechanism of deformation and material removal, to rank the materials according to their abrasion resistance, and to measure scratch hardness. In this method, a hard element called indenter is used to generate a groove in the surface. The load is applied by weight. Wear of test specimens was determined by the scratch width after the scratch is carried out. In metallurgy, hardness is defined as the ability of a material to resist plastic deformation. Hardness covers several properties: resistance to deformation, resistance to friction and abrasion. There is no definite relation between hardness, as measured by the Brinell hardness testing method, and wear. In general, a high Brinell hardness number may be expected to indicate a metal, which will give had better wear, there are so many exceptions that this test for indication wearing properties would be unreliable. Metallurgical mounts are generally made of a cross section through a material. The piece is cut in cross section and mounted in a suitable medium. The mount is then polished to a mirror finish, etched in order to reveal its microstructure then be viewed via optical and electron microscopy. Often it is necessary to etch the sample in order to reveal its microstructure.

III. Results and Discussions

A. Corrosion Mediums

Fig. 1 shows the effect of the corrosion mediums on the corrosion rate of carbon steel at various concentrations and test periods. It is clear that the effect of DSO is higher than DMT at the two concentrations. The effect of the scratch load on the scratch width at various test periods is shown in Figs. 2 and 3. It is clear that as the scratch load increases, the scratch width increases due to the increment of the applied force on the area. As the corrosion rate of DSO is higher compared to DTU, so, the DSO trends have higher scratch width at all concentrations in agreement with [5]. Due to the severe attack of DSO compared to DTU, it weakens the surface layers of the mild steel material that results in the strength and hardness decrement. Fig. 4 shows that the BHN difference variations before and after the exposure to the corrosion mediums of 0.8 mg. The increment of BHN is due to the deposition of the hardened corrosion layer on the mild steel surface. As DMD is more attackers to the surface, DBT BHN difference variation trend is shown higher than DMD trend in agreement with [12].

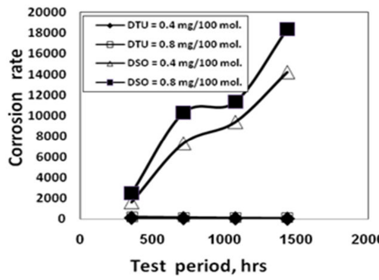


Fig. 1 Corrosion rate /test period relations at various sulphur compound types and concentrations

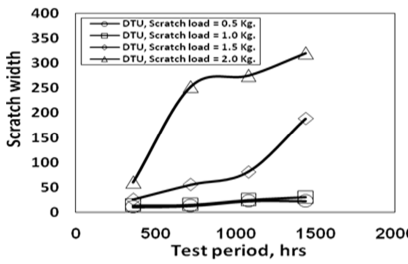


Fig. 2 Scratch width ($x10^{-3}$μm) / test period relation at various scratch loads of DTU

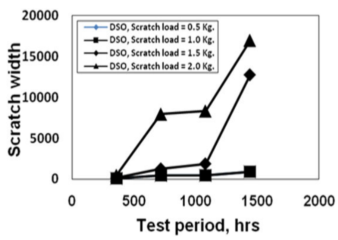


Fig. 3 Scratch width ($x10^{-3}$ μm) / test period relation at various scratch loads of DSO

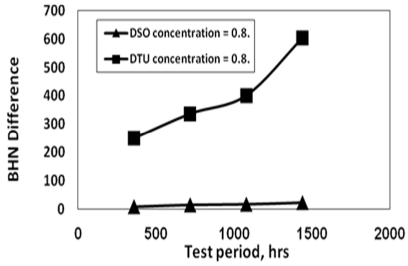


Fig. 4 BHN difference / test period relation at 0.8 concentrations

B. Corrosion Inhibitors

Figs. 5 and 6 illustrate the effect of the natural inhibitor types and concentrations on the inhibitor efficiency at both DTU and DSO corrosion mediums of 0.8 mg/100 ml technical white oil. It is clear that the natural inhibitors efficiency trends using the DSO corrosion medium are located higher due to the higher corrosion rate of DSO compared to DTU, as shown in Fig. 1. In addition, it is clear that as the inhibitor concentration increases, the inhibitor efficiency increases due to the inhibitive effect increment in acceptance with [12]. The figures show that the Eruca Sativa extracts trends are found higher followed by Rosell Peels trends and Mango Peels trends, respectively, at various concentrations. As the test period increases, the inhibition effect of the three inhibitors increases for all concentrations in agreement with the previous publications [1].

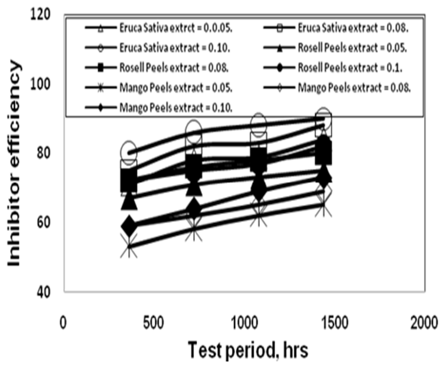


Fig. 5 Natural inhibitors efficiency (%) / test period relation at 0.08 DTU medium

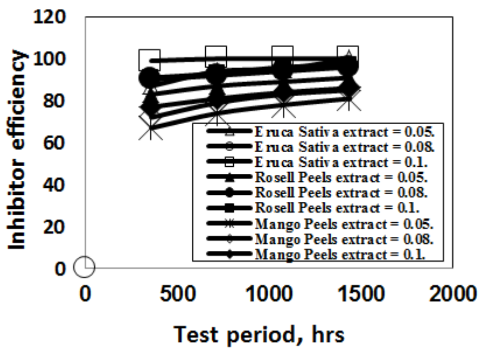
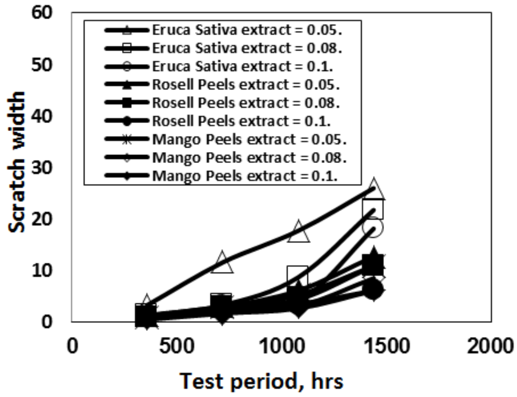
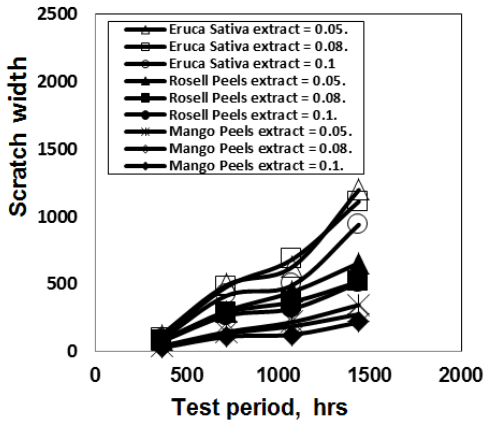


Fig. 6 Natural inhibitors efficiency (%) / test period relation at 0.08 DSO medium

Figs. 7 (a) and (b) illustrate the variation of the scratch width x10^{-3}μm with the scratch loads of 2.0 Kg at various test periods for the three natural inhibitors at 0.8 concentration at the two corrosion mediums DTU and DSO with 0.08 mg/100 ml of technical white oil. For all natural inhibitors, it is clear that as the test period increases, the scratch width increases due to the longest exposure [2]. In addition, as the inhibition concentration increases, the scratch width increases due to the previous explanation for all natural inhibitors. The figures show that the higher inhibition efficiency, the higher scratch width and the lower BHN in agreement with [1]. According to that, the figures show that the Eruca Sativa extract that had the higher inhibition effect had the larger scratch width while the Mango Peels extract that had the lowest inhibition effect.



(a) DTU at 2.0 Kg



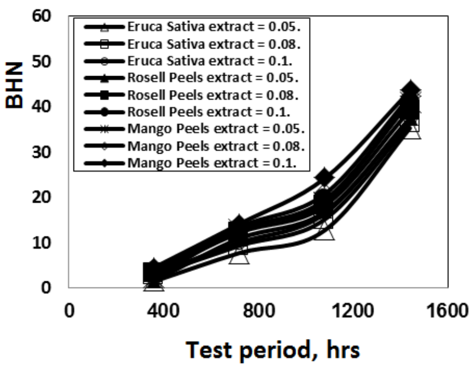
(b) DSO at 2.0 Kg

Fig. 7 Variation of scratch width with test periods at 0.8 corrosion mediums concentration

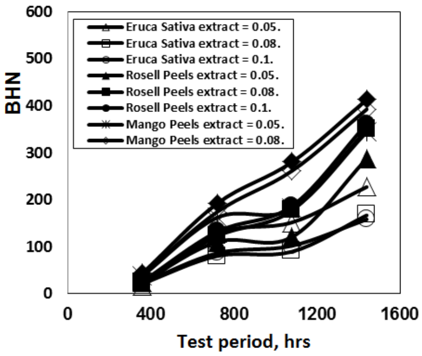
Figs. 8 (a) and (b) show that the BHN of both DTU and DSOl. DTU that had the lowest corrosion effect had the lower BHN than that of DSO and the Mango Peels inhibitor that had the lowest inhibition effect had the higher BHN values in agreement with [12] and the results shown in Figs. 6 and 7.

C. Structure Examination

Fig. 9 shows the SEM micrographs of different slides of mild steel after immersion in the aqueous solutions of DTU and DSO corrosion mediums. Fig. 9 (a) shows the micrographs by SEM of the unexposed surface of the uncorroded surface of mild steel which is found to be absolutely free from any noticeable defect such as cracks and pits. Polishing scratches are also visible. While Fig. 9 (b) shows, that DTU has no noticeable effect on the mild steel corrosion. Fig. 9 (c) shows that the micrograph exhibited a cocoon-like structure for solution with the absence of the inhibitors. This explains the fact that the surface was already undergoing a localized attack, which resulted in a cocoon-like structure. It is clear that the upraising value of O is due to the formation of the ferrous hydroxide, whereas, for C, it is due to the presence of catching that acts as the active inhibitor and complexes with the mild steel surface [6]. Fig. 10 illustrates the effect of the natural inhibitor on the corroded mild steel specimens. Fig. 10 (a) shows the effect of the Eruca Sativa extract on the inhibition of the corroded specimen. It is found to be free from any noticeable defect such as cracks and pits. Polishing scratches are also visible. Figs. 10 (b) and (c) show micrographs by SEM of carbon steel specimens exposed in 0.08 DSO solutions at a magnification of 750. Uniform corrosion was observed. Flakes showing corrosion products are observed in the micrographs. The electron micrographs, Fig. 10 (c), reveal that the surface was strongly damaged owing to corrosion in absence of the inhibitor effect, but in Fig. 10 (b), due to the presence of inhibitor there is a much less damage on the surface. This is attributed to the formation of a good protective film on the carbon steel surface.



(a) BHN at 0.8 DTU concentration



(b) BHN at 0.8 DSO concentration

Fig. 8 Variation of BHN with test periods at 0.8 corrosion mediums concentration

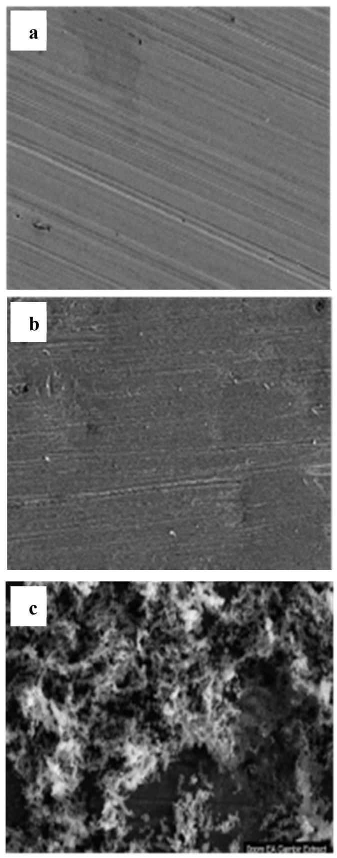


Fig. 9 Micrographs of carbon steel in (a) fresh steel, (b) 0.8 DTU, and (c) 0.8 DSO (750X & 360 hrs)

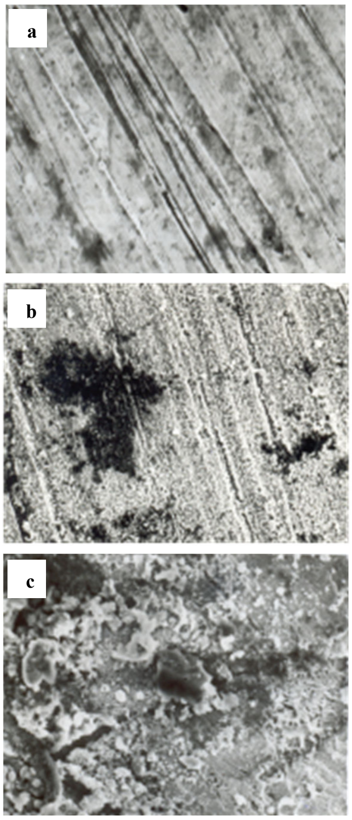


Fig. 10 Micrographs of corroded carbon steel specimens in (a) 0.1 Eruca Sativa extract, (b) 0.1 Rosell Peels extract, and (c) Mango Peels extract with 0.8 DSO (750X and 360 hrs)

IV. Conclusions

The following conclusions are obtained;

1. The DSO has the higher corrosion rate compared to DTU.
2. As the corroded mediums concentrations and exposure time increases, the corrosion rate increases.
3. The Eruca Sativa extract have a higher inhibition effect followed by Rosell Peels and Mango Peels extracts.
4. The higher inhibition efficiency, the higher scratch width and the lower BHN.
5. The metallographic examination is in a good agreement with the experimental results.

References

[1] E. A. Noor, and A. Al-Moubaraki, "Corrosion Behavior of Mild Steel in Hydrochloric Acid Solutions", Int. J. Electrochem. Sci., 3, pp. 806-818, 2008.

[2] P. Matheswaran and A. K. RAMASAMY, "A Study of Mild Steel Corrosion Using Adhatoda Vasica (AV) Extract as Inhibitor in Different Acid Medium", E-Journal of Chemistry, 7(4), pp. 1284-1289, 2010.

[3] Ashraf T. Mohamed and Hala M. Abo-Dief, " Natural Corrosion Treatment Of Mild Steel Pipelines", The International Engineering Conference on Hot Arid Regions (IECHAR 2010), Al-Ahsa, KSA, pp. 263-269, May 1-2, 2010.

[4] Ashraf T. Mohamed, and Hala M. Abo-Dief "Effect of The Exposure Period in The Carbon Steel Corrosion using Organic Sulfur Compounds", The Fourteenth Asian-Pacific Corrosion Control Conference (14APCCC), Shanghai, P R China, 21-24 October, 2006.

[5] H.A. Abo Dief, E.A. Eissa, S.T. Keera and A.R. Taman, " Study of Carbon Steel Corrosion in Sulphur Media", J.l of Applied Sciences Research, 6(8): 1325-1333, 2010.

[6] M. Liang, "Theoretical Elucidation on the Corrosion Tube Growth Mechanism of Mild Steel in the Effect of PH on Oxygen Corrosion at Elevated Pressures", Journal of Marine Science and Technology, Vol. 16, No. 4, pp. 265-270, 2008.

[7] N.S. Patel, S. Jauhari and G.N. Mehta, "The Inhibition of Mild Steel Corrosion in 1 N HCl by Imidazole Derivatives", Acta Chim. Slov, Vol. 57, pp. 297-307, 2010.

[8] Ashraf T. Mohamed, H.M. Abo-Dief, Fahd A. Al-Zahrani, and A.E. Sayed, "Analytical and Experimental Investigation of Trussed Aluminium Composites Wear", The International Conference on Mechanical and Industrial Engineering (ICMIE 2010), Singapore, August 25-27, 2010.

[9] N. O. Eddy, S. A. Odoemelam and P. Ekwumemgbo, "Inhibition of the Corrosion of Mild Steel in H2SO4 by Penicillin G", Scientific Research and Essay Vol. 4 (1), pp. 033-038, January, 2009.

[10] M. T. Liang, "Theoretical Elucidation on the Corrosion Tube Growth Mechanism of Mild Steel In The Effect of Ph on Oxygen Corrosion AT Elevated Pressures", Journal of Marine Science and Technology, Vol. 16, No. 4, pp. 265-270, 2008.

[11] K. Parameswari, S. Rekha, S. Chitra, and E. Kayalvizhy, " Study on the Inhibition of Mild Steel Corrosion by Benzoisoxazole and Benzopyrazole Derivatives in H_2SO_4 Medium", Portugaliae Electrochimica Acta, Volume 28(3), pp. 189-201, 2010.

[12] N. O. Eddy, P. Ekwumemgbo1 and S. A. Odoemelam, " Inhibition of the corrosion of mild steel in H2SO4 by 5-amino-1-cyclopropyl-7-{(3R, 5S) 3, 5-dimethylpiperazin- 1-YL} -6, 8-difluoro-4-oxo-uinoline-3-carboxylic acid (ACPDQC)", International Journal of Physical Sciences Vol. 3 (11), pp. 275-280, November, 2008.